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A CRAMPS and 13C CP/ MAS NMR Examination of Solid-Solid Transitions in n-Hexatriacontane (C36H74)

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The normal paraffins can undergo several transitions before melting[1] and may thus serve as interesting model compounds for polyethylene, which also undergoes solid-solid transitions, the strongest and best-known being the so-called α transition. Our examination of n-hexatriacontane (C36) has been greatly furthered by the use of the solid-state 1H NMR technique known as CRAMPS (Combined Rotation And Multiple Pulse Spectroscopy).[2] This technique, combined with DSC and 13C CP/MAS NMR, has allowed us to make tentative assignments for the molecular motions occurring at different temperatures below the melting point.

DSC of C36 crystallized by various methods at several cooling rates displays several different patterns of endothermic transitions in the solid phase; depending on the sample treatment, as many as three solid-solid or "premelt" transformations can be seen to occur. DSC measurements were conducted on these samples using a TA Instruments Model 2920 DSC in standard mode with a heating rate of 0.5 °C/minute in a nitrogen atmosphere. NMR measurements were conducted on a Bruker MSL-400 spectrometer (400.13 MHz 1H, 100.043 MHz 13C) using standard and high-temperature Bruker double-air-bearing magic-angle-spinning (MAS) probes. 13C spectra were collected at approximate 1 K thermal intervals using cross-polarization (CP) and MAS. 13C experimental times were shortened by the use of a flipback pulse (negative 90° 1H pulse). CRAMPS spectra were acquired using the BR24 pulse sequence.[3]

A representative DSC trace of a melt-crystallized C36 sample is shown in Figure 1. This sample was heated above the melt in the DSC, then the sample pan was removed and placed on a room-temperature aluminum sheet. Two large transitions, corresponding to the transition to the pseudohexagonal or "rotator" phase (72.73 °C) and to the melting transition (74.94 °C), are readily apparent. Also visible are two smaller premelt transitions (70.72 and 69.93 °C) that become more defined upon enlargement of the thermogram.

The DSC thermogram of the other applied sample treatment is shown in Figure 2. The sample was melted in a small beaker in a water bath, then poured into liquid nitrogen, collected, dried, and placed in a DSC sample pan. Note that the melting (75.0 °C), pseudohexagonal (72.73 °C), and smaller premelt (70.24 °C) transition are very similar to those seen in Figure 1. In fact, the premelt transition seen here appears to be a combination of the two premelt transitions seen in Figure 1. By correlating the thermal transitions seen in these DSC spectra with the solid-state NMR spectra for the same sample treatments, it is possible to assign types of molecular motions to each of the transitions.

Figure 3 shows a stack plot of significant spectra in the variable-temperature 13C CP/MAS series for a sample treatment similar to that of the sample whose DSC thermogram is shown in Figure 1. The 25.8 °C spectrum displays two broad methyl peaks, at 14.8 and 15.2 ppm. Both of these are also present in the 66.8 °C spectrum, but only a sharp 14.8 ppm methyl peak remains at 70.8 °C. This peak gradually drifts upfield and sharpens a bit more, reaching 14.4 ppm in the pseudohexagonal phase at 73.0 °C. The α-

CH2 peak behaves similarly, a broad, low 24.9 ppm peak at 25.8 °C which sharpens and moves upfield to 24.6 ppm at 70.8 °C, where one can see evidence of a shoulder peak growing in on the upfield side of the peak. By 71.6 °C, all of the α-CH2 resonance has moved to this upfield chemical shift (24.0 ppm).

The changes in both the methyl and α-CH2 resonances are non-cooperative transitions: i.e., a gradual transfer occurs between discrete states, without a significant chemical shift change in either of the peaks. The examples of this phenomenon are the two methyl peaks changing intensity from 25.8-70.8 °C and the intensity change in the α-CH2 peaks over the 66.8-71.6 °C range.

The all-trans -CH2- peak at 32.9 ppm also narrows with increasing temperature, and shoulder peaks begin to be seen at 70.8 °C, just before the pseudohexagonal transition. Upon entry into the pseudohexagonal phase, the internal methylene peak narrows sharply and moves downfield to 33.3 ppm, showing two peaks that were hidden beneath it: the γ-CH2 (31.9 ppm) and δ-CH2 (32.4 ppm) peaks.

Significant spectra from the CRAMPS variable-temperature series are shown in Figure 4, along with text showing the correlations between the changes seen in the CRAMPS spectra and transitions observed in the DSC thermograms and 13C spectra. These spectra clearly show the peak resolution of the CRAMPS technique, and the advantage of this technique over standard MAS 1H NMR is easily seen. Close correlation with 13C and DSC transitions is observed. The disappearance of the methyl peak at 0 ppm (NOTE: chemical shifts are unreferenced, and the largest peak, which we assign to the main-chain -CH2- protons and appears to be consistent in all spectra, was arbitrarily set at 1.2 ppm.) between 55.5 and 66.0 °C correlates with the baseline shift seen in DSC (see below) and small chemical shift changes in the upfield methyl and α-CH2 peaks. A narrowing of the internal -CH2- peak between 69.2 and 70.0 °C is assigned to greater chain freedom associated with the onset of the DSC premelt transitions.

Between 71.7 and 73.5 °C, the CRAMPS spectra show entry into the pseudohexagonal phase, as seen by the appearance of two downfield shoulder (1.4 and 1.8 ppm) on the internal -CH2- peak and baseline resolution of the internal -CH2- and methyl (0.8 ppm) peaks. These shoulder peaks continue to become more defined until the melting transition between 76.5 and 79.7 °C, at which point the 1.4 ppm shoulder peak on the internal -CH2- peak diminishes greatly and the 1.8 ppm peak increases in intensity. A third shoulder peak at 1.3 ppm may be discerned in the 76.5 °C spectrum. We have not as yet been able to assign these peaks to specific molecular motions, but the correlation with the 13C and DSC data encourages the conclusion that the changes in the CRAMPS spectra reflect the same transitions.

It is perhaps easier to see the correlation between the chemical shift changes in the 13C CP/MAS spectra and thermal transitions by looking at Figure 5, which overlays the chemical shift peak values from collected CP/MAS spectra onto a greatly enlarged rendition of the thermogram from Figure 1. At this level of enlargement, another previously unseen DSC transition is observed at approximately 58 °C, which may correlate with an approximately ± .1 ppm oscillation in the α-CH2 peak chemical shift seen from 50 to 60 °C.

Another item of note observed from Figure 5 is that changes in chemical shift occur at the onset of thermal transitions in the DSC. Perhaps the most obvious point at which this occurs is at the pseudohexagonal transition. NMR onset (discontinuities in the all-trans region near 30 ppm and in the α-CH2 region near 25 ppm) for this transition is 72.2 °C, which correlates well with the DSC onset of 72.1 °C. Following this argument, the disappearance of the downfield methyl peak and a slight upfield shift (0.1 ppm)of the upfield methyl peak may be correlated with the onset of the DSC transition that peaks at 69.9 °C.

It can be seen that CRAMPS NMR represents a valuable addition to available characterization techniques. Work is currently in progress in our group to apply CRAMPS to other sample treatments of C36 to gain a better, more comprehensive understanding of the premelt transitions in this material.

Acknowledgements

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Figure 1 DSC thermogram of hexatriacontane melt-quenched onto room-temperature aluminum sheet.
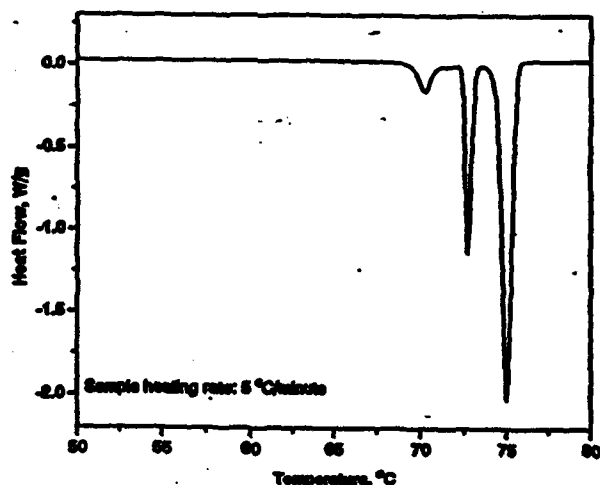

Figure 2 DSC thermogram of hexatriacontane melt-quenched into liquid nitrogen.
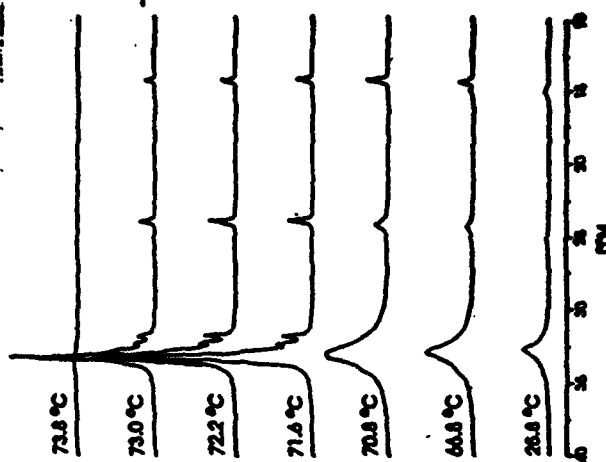

Figure 3 Significant spectra from the variable-temperature ^{13}C CP/MAS experiment series.
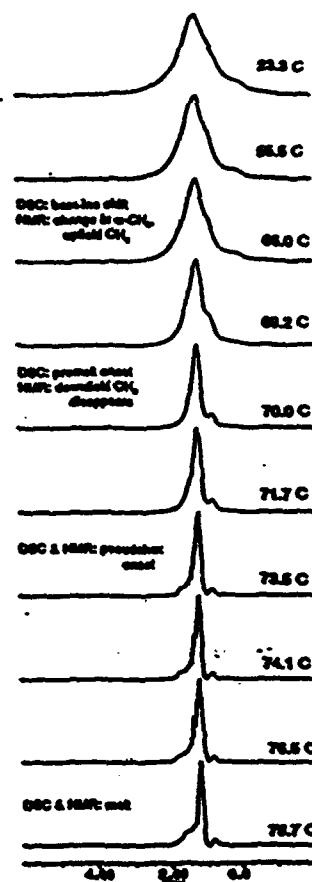

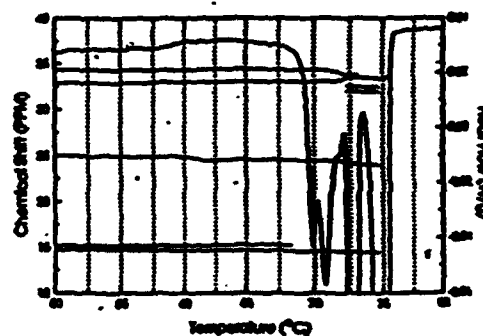Figure 4 Spectra from the variable-temperature CRAMPS experiment series.

Figure 5 Correlation of peak chemical shift values from variable-temperature ^{13}C CP/MAS with DSC thermal transitions of the same sample treatment.